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(54) DETERGENT COMPOSITIONS HAVING IMPROVED SOIL RELEASE PROPERTIES

(71) We, THE PROCTER & GAMBLE COMPANY, a Corporation organised under the laws of the State of Ohio, United States of America of 301 East Sixth Street, Cincinnati, Ohio 45202, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:—

This invention relates to detergent compositions and to a method for simultaneously laundering and conferring soil release properties to textile materials. More specifically, the present compositions comprise mixtures of surfactants and specific, highly substituted methyl cellulose soil-release agents.

The use of various coating agents to improve cleaning performance by modifying the surface of fabrics is known in the art. Such soil-release coatings facilitate and improve fabric cleaning during subsequent laundering operations. Many such soil-release materials are ester polymers which are prepared from benzenoid petroleum distillates; see, for example, British Patents 1,088,984 and 1,092,435. Other soil-release materials are not based on petroleum, but rather employ cellulose as the backbone of the fabric treatment polymer.

U.S. Patent 3,668,000 relates to a method for improving soil-release characteristics of textiles by means of hydroxypropylmethylcellulose.

U.S. Patent 3,435,027 relates to the preparation of acylated derivatives of carboxymethylcellulose, carboxymethylhydroxyethylcellulose, hydroxyethylcellulose, hydroxypropylcellulose, methylcellulose and methylhydroxypropylcellulose and their use in a broad range of applications, including warp sizings.

The "CELLULOSE GUM CATALOG", Hercules Powder Company, describes the application of carboxymethylcellulose to fabrics in home laundering operations as a size or finish and mentions that such treatment contributes to easier soil removal during subsequent washing.

The "METHOCEL PRODUCT INFORMATION" data sheets, Dow Chemical Company, 1966, disclose hydroxybutylmethylcellulose (HBMC) and several uses for this cellulose derivative. Published South African Patent 71/5149 teaches the use of HBMC in detergent compositions.

U.S. Patent 2,663,989 discloses "conditioning compositions" for yarns, fabrics, and the like which can be applied from stable aqueous media. Such compositions contain various cellulose derivatives such as carboxymethylcellulose, methylcellulose and hydroxyethylcellulose, as well as stabilizers and dispersants such as nonionic surfactants. The compositions are applied to textiles by passage through an aqueous bath.

U.S. Patent 2,994,665 discloses heavy-duty liquid detergent compositions containing a pair of soil-suspending cellulose derivatives. U.S. Patent 3,523,088 teaches soil-suspending pairs of cellulose derivatives in detergent compositions.

British Patent 1,171,877 discloses the use of hydroxyalkylated starch and cellulose derivatives in combination with terephthalate polymers to provide soil release coatings to fabrics.

British Patent 1,045,197 relates to textile sizing agents containing water-soluble cellulose ethers in combination with polyalkylene glycol.

As can be seen from the foregoing, there is a continuing search for soil-release agents of all types. In view of the current shortage of petrochemicals, it would be especially advantageous to provide soil-release polymers which are not based on petroleum feedstocks. The cellulose ethers are one readily available type of fabric-finishing polymers.

The prior-art cellulose-based soil-release fabric finishes are deficient in that their efficacy varies with fabric type. For example, a given cellulosic finishing agent may impart satisfactory soil-release properties to polyester/cotton blends but not to pure polyester fibers. Moreover, certain cellulose derivatives must be padded onto fabrics at the mill and are not useful in detergent compositions designed for use in the home. Other finishing agents require multiple applications to the fabric surfaces before a truly effective soil-release finish is obtained.

According to the present invention, a detergent composition having soil-release properties comprises:

(a) from 5% to 99% by weight of a water-soluble organic surfactant selected from anionic, nonionic, zwitterionic and ampholytic surfactants and mixtures thereof, and

(b) at least 0.05% by weight of a methyl cellulose ether having a D.S. methyl of at least 2.1, provided that when the composition is in liquid form, the methyl cellulose must have a viscosity of from 20 to 250 centipoises.

Preferably the compositions of this invention comprise from 10% to 35% by weight of the organic surfactant (a) and from 0.25% to 1.5% by weight of the methyl cellulose ether (b).

Thus, the present invention enables the production of detergent compositions having soil-release agents based on cellulosic, rather than petrochemical, feedstocks, which compositions can be used simultaneously to clean and impart soil-release properties to fabrics, especially to a wide range of polyester fabrics including polyester/cotton blends.

The compositions herein can optionally contain up to 94.55% by weight of various fillers, carriers and detergency builders commonly used in detergent compositions.

The present invention also provides a method for concurrently cleansing and imparting soil-release properties to fabrics by contacting said fabrics with an aqueous laundering medium containing from 500 ppm to 10,000 ppm of a composition of this invention.

The detergent compositions of the present invention comprise several components, each of which is described hereinafter.

A. Surfactant

Water-soluble surfactants used in the present composition include any of the common anionic, nonionic, ampholytic and zwitterionic detergent agents well known in the detergent arts. Mixtures of surfactants can also be employed herein. More particularly, the surfactants listed in U.S. Patent 3,332,880 can be used herein. Non-limiting examples of surfactants suitable for use in the present compositions and methods are as follows.

Water-soluble salts of the higher fatty acids, i.e. "soaps" are useful as the anionic surfactant herein. This class of surfactants includes ordinary soaps such as the alkali metal (e.g. sodium and potassium), ammonium and alkanolammonium salts of higher fatty acids containing from about 8 to about 24 carbon atoms and preferably from about 10 to about 20 carbon atoms. Soaps can be made by direct saponification of fats and oils or by the neutralization of free fatty acids. Particularly useful are the sodium and potassium salts of the mixtures of fatty acids derived from coconut oil and tallow, i.e., sodium or potassium tallow and coconut soap.

Another class of anionic surfactants includes water-soluble salts, particularly the alkali metal, ammonium and alkanolammonium salts, of organic sulfuric reaction products having in their molecular structure an alkyl group containing from about 8 to about 22 carbon atoms and a sulfonic acid or sulfuric acid ester group. (Included in the term "alkyl" is the alkyl portion of acyl groups). Examples of this group of synthetic surfactants which can be used in the present invention are the sodium and potassium alkyl sulfates, especially those obtained by sulfating the higher alcohols (C_8-C_{18} carbon atoms) produced by reducing the glycerides of tallow or coconut oil; and sodium and potassium alkyl benzene sulfonates, in

which the alkyl group contains from about 9 to about 15 carbon atoms, in straight chain or branched chain configuration, e.g., those of the type described in U.S. Patents 2,220,099 and 2,477,383. Especially valuable are linear straight chain alkyl benzene sulfonates in which the average of the alkyl groups is about 13 carbon atoms, abbreviated as C₁₃LAS.

Other anionic surfactant compounds herein include the sodium alkyl glyceryl ether sulfonates, especially those ethers of higher alcohols derived from tallow and coconut oil; sodium coconut oil fatty acid monoglyceride sulfonates and sulfates; and sodium or potassium salts of alkyl phenol ethylene oxide ether sulfate containing about 1 to about 10 units of ethylene oxide per molecule and wherein the alkyl groups contain about 8 to about 12 carbon atoms.

Other useful anionic surfactants herein include the water-soluble salts of esters of α -sulfonated fatty acids containing from 6 to 20 carbon atoms in the ester group; water-soluble salts of 2-acyloxy-alkane-1-sulfonic acids containing from 2 to 9 carbon atoms in the acyl group and from 9 to 23 carbon atoms in the alkane moiety; alkyl ether sulfates containing from 10 to 20 carbon atoms in the alkyl group and from 1 to 30 moles of ethylene oxide; water-soluble salts of olefin sulfonates containing from 12 to 24 carbon atoms; and β -alkyloxy alkane sulfonates containing from 1 to 3 carbon atoms in the alkyl group and from 8 to 20 carbon atoms in the alkane moiety.

Preferred water-soluble anionic organic surfactants herein include linear alkyl benzene sulfonates containing from 11 to 14 carbon atoms in the alkyl group; the tallow range alkyl sulfates; the coconut range alkyl glyceryl sulfonates; alkyl ether sulfates wherein the alkyl moiety contains from 14 to 18 carbon atoms and wherein the average degree of ethoxylation varies between 1 and 6; the sulfated condensation products of tallow alcohol with from 3 to 10 moles of ethylene oxide; olefin sulfonates containing from 14 to 16 carbon atoms; and soaps, as hereinabove defined.

Specific preferred anionic surfactants for use herein include: sodium linear C₁₀—C₁₈ alkyl benzene sulfonate; triethanolamine C₁₀—C₁₈ alkyl benzene sulfonate; sodium tallow alkyl sulfate; sodium coconut alkyl glyceryl ether sulfonate; the sodium salt of a sulfated condensation product of a tallow alcohol with from about 3 to about 10 moles of ethylene oxide; and the water-soluble sodium and potassium salts of higher fatty acids containing 8 to 24 carbon atoms.

It is to be recognized that any of the foregoing anionic surfactants can be used separately herein or as mixtures. Examples of preferred anionic surfactant mixtures herein are as follows.

An especially preferred alkyl ether sulfate detergent component useful in the present compositions and processes is a mixture of alkyl ether sulfates, said mixture having an average (arithmetic mean) carbon chain length within the range of from 12 to 16 carbon atoms, preferably from 14 to 15 carbon atoms, and an average (arithmetic mean) degree of ethoxylation of from 1 to 4 moles of ethylene oxide, preferably from 2 to 3 moles of ethylene oxide; see British Patent Specification 1,408,969.

Specifically, such preferred mixtures comprise from 0.05% to 5% by weight of mixture of C₁₂₋₁₃ compounds, from 55% to 70% by weight of mixture of C₁₄₋₁₅ compounds, from 25% to 40% by weight of mixture of C₁₆₋₁₇ compounds and from 0.1% to 5% by weight of mixture of C₁₈₋₁₉ compounds. Further, such preferred alkyl ether sulfate mixtures comprise from 15% to 25% by weight of mixture of compounds having a degree of ethoxylation of zero, from 50% to 65% by weight of mixture of compounds having a degree of ethoxylation from 1 to 4, from 12% to 22% by weight of mixture of compounds having a degree of ethoxylation from 5 to 8 and from 0.5% to 10% by weight of mixture of compounds having a degree of ethoxylation greater than 8.

Preferred "olefin sulfonate" surfactant mixtures utilizable herein comprise olefin sulfonates containing from about 10 to about 24 carbon atoms. Such materials can be produced by sulfonation of α -olefins by means of uncomplexed sulfur dioxide followed by neutralization under conditions such that any sulfonates present are hydrolyzed to the corresponding hydroxy-alkane sulfonates. The α -olefin starting materials preferably have from 14 to 16 carbon atoms. Said preferred α -olefin sulfonates are described in U.S. Patent 3,332,880.

Semi-polar surfactants useful herein include water-soluble amine oxides containing one alkyl moiety of from 10 to 28 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from 1 to 3 carbon atoms; water-soluble phosphine oxides containing one alkyl moiety

of 10 to 28 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from 1 to 3 carbon atoms; and water-soluble sulfoxides containing one alkyl moiety of from 10 to 28 carbon atoms and a moiety selected from the group consisting of alkyl and hydroxyalkyl moieties of from 1 to 3 carbon atoms.

Ampholytic surfactants include heterocyclic secondary and tertiary amines substituted by aliphatic radicals in which the aliphatic moiety can be straight chain or branched and wherein one of the aliphatic substituents contains from 8 to 18 carbon atoms and at least one aliphatic substituent contains an anionic water-solubilizing group.

Zwitterionic surfactants include derivatives of aliphatic quaternary ammonium, phosphonium and sulfonium compounds in which the aliphatic moieties can be straight or branched chain, and wherein one of the aliphatic substituents contains from 8 to 18 carbon atoms and one contains an anionic water solubilizing group.

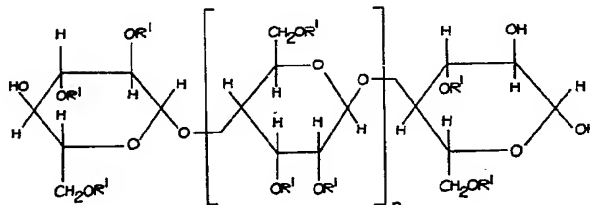
Nonionic surfactants include the water-soluble ethoxylates of C_{10} — C_{20} aliphatic alcohols and C_6 — C_{12} alkyl phenols. Many nonionic surfactants are especially suitable for use as suds controlling agents in combination with anionic surfactants of the type disclosed herein.

It is to be recognized that mixtures of the foregoing surfactants are also useful herein.

B. Soil Release Agent

The soil release fabric finishing agents employed in the present compositions are the methyl ethers of cellulose having a high degree of methyl substitution (DS methyl). More specifically, the high-DS methyl cellulose ethers herein can be characterized as cellulose having at least 2.1, preferably from 2.1 to 2.8, methyl groups, R' , on the hydroxyls of the anhydroglucose units of cellulose, i.e., a DS of from 2.1 to 2.8. It has now been discovered that these high DS methyl cellulose derivatives exhibit heretofore unrecognized advantages as oily soil release fabric finishes and are far superior to the lower DS methyl and the various hydroxyalkyl cellulose known in the art.

The basic structure of the cellulose methyl ethers herein is as follows, wherein group R' is methyl. In the formula the integer, n , typically averages from about 100 to about 10,000.



When preparing the alkyl cellulose ether soil release agents employed in the present compositions the hydroxyl groups of the anhydroglucose units of cellulose are reacted with a methylating agent, thereby replacing the hydrogen of the hydroxyls with methyl. The number of substituent methyl groups can be designated by weight percent, or by the average number of methyl (i.e., as methoxyl) groups on the anhydroglucose units, i.e., the DS. If all three available positions on each anhydroglucose unit are substituted, the DS is designated three (3); if an average of two $-OH$'s are substituted, the DS is designated two (2), etc.

Commercial processes for preparing methyl cellulose ethers involve, for example, simply combining methyl chloride with a cellulose feed stock of the type disclosed hereinafter under alkaline conditions. Such a process results in a DS of below 2, and most generally a DS of about 1.5. The prior-art materials taught for use as fabric finishes are those having a low DS, i.e., a DS below 2, and usually below about 1.5. These lower DS materials are apparently specified for use as fabric finishes inasmuch as they are commercially available and have what was heretofore thought to be the requisite high water-solubility properties necessary for sorption on fabric surfaces. It is to be understood that the methyl halides used to prepare the high-DS methyl celluloses herein can contain minor amounts of other alkyl halides. The resulting cellulose ethers will, of course, contain very

minor proportions of the corresponding alkyl groups. This is not important to the invention herein.

In contrast with the prior art teachings regarding the cellulosic fabric finishes, the soil release agents for use herein have a degree of methyl substitution in the range of from 2.1 to 2.8, preferably from 2.2 to 2.7, most preferably from about 2.3 to 2.6.

Of course, the theoretical DS limit is 3.0, inasmuch as there are a maximum of 3 hydroxyl groups on each anhydroglucose unit in cellulose. Surprisingly, the high DS, methyl cellulose ethers herein are sufficiently water soluble to provide good soil release fabric finishes when applied from an aqueous bath. Moreover, the high DS, methyl cellulose ethers exhibit their superior oily soil release properties when applied to fabrics from a detergent composition.

The high DS methyl cellulose ethers herein can be prepared by the exhaustive methylation of cellulose using a methyl halide, preferably methyl chloride, and caustic, preferably sodium hydroxide, in a pressure vessel in the manner well-known in the art for preparing the lower DS methyl celluloses. However, the methylation procedure can be simply repeated and continued until the high DS materials are secured. The progress of the methylation reaction can be monitored by periodically sampling the reaction product and determining the degree of methoxylation in the manner more fully disclosed hereinafter.

It is to be understood that detergent compositions containing any of the high DS methyl cellulose materials used herein exhibit excellent oily soil removal properties compared with most low DS (i.e., DS below about 2) alkyl and hydroxyalkyl celluloses known in the art. From the standpoint of oily soil removal, the most highly preferred high DS methyl cellulose ethers herein are those characterized by a gel point in an aqueous solution below 50°C, preferably in a range of from about 25°C to about 48°C. While not intending to be limited by theory, it appears that the high DS methyl celluloses having gel points below 50°C, and preferably in the recited range, interact with, and deposit on, fabrics from an aqueous laundry bath in optimal fashion under normal laundry conditions. The gel point of the cellulose soil release ethers herein can be determined in the manner disclosed more fully hereinafter.

The highly preferred methyl celluloses for use herein are characterized by their high DS and gel point as specified hereinabove, and can be further characterized by a solution viscosity above 20 centipoise, more preferably above 40 centipoise (cps). It is to be recognized that the solution viscosities of the cellulose ethers herein can vary over an extremely wide range, and are often as high as 70,000 (measured as a 2% wt. solution in water). The viscosity of the preferred cellulosic derivative herein can be determined in the manner set forth in ASTM Standard D—2363, more fully described hereinafter.

In addition to the foregoing parameters, the most highly preferred high DS methyl celluloses can be further characterized as having a weight average degree of polymerization of greater than 100, more preferably from 100 to 1000, most preferably from 400 to 800. The term "weight average degree of polymerization" used herein to define the most highly preferred high DS methyl celluloses relates to the average number of anhydroglucose units in the cellulose polymer. The weight average degree of polymerization (DP_w) is related to such physical parameters of the cellulose polymer as solubility, gel point and viscosity. The DP_w of the high DS methyl celluloses herein can be determined by measuring their solubility in cadoxen in the manner described hereinafter and calculating the DP_w using the relationship of Henley, as set forth in the review article by W. J. Brown, *TAPPI*, 49, 367 (1966).

High DS methyl cellulose soil release agents of the type employed herein having the most preferred DP_w range can be prepared using cotton linters or wood-derived cellulose feedstock. It is well known that cotton-based cellulose material has a DP_w greatly in excess of 1000. However, the caustic treatment during methylation reduces the DP_w due to the action of the caustic on the cellulose polymers. Accordingly, cotton is a perfectly acceptable source of cellulose when preparing the high DS materials falling within the preferred DP_w ranges cited herein. Wood-derived cellulose is known to be comprised of cellulose polymers having a DP_w of about 2000, and below. Accordingly, wood-based cellulose can easily be converted to the high DS methyl materials having the preferred DP_w range recited hereinabove without the need for any additional degradation, although some degradation will occur on contact with the caustic.

Specific examples of especially useful cellulose soil release agents of the type

disclosed for use in detergent compositions in the manner of this invention are set forth hereinafter in Tables 1 and 2.

C. Optional Additives

The detergent compositions herein can optionally contain various additive materials commonly employed in detergent compositions.

Detergency builders are especially useful additives and can be used at concentrations of from about 10% to about 80%, preferably from about 25% to about 70%, by weight of the total compositions. As will be described more fully hereinafter, such detergency builder materials are especially useful when spray-drying granular detergent compositions containing the cellulosic soil release materials herein by virtue of their ionic electrolyte properties. Builder electrolytes useful herein include any materials which, in addition to dissolving and ionizing in water, provide a detergency enhancing, i.e., "building", effect.

Examples of detergency builders include the water-soluble salts, especially the alkali metal salts, of pyrophosphates, orthophosphates, polyphosphates, phosphonates, carbonates, polyhydroxysulfonates, silicates and polyacetates. Specific examples of inorganic phosphate builders include sodium and potassium tripolyphosphates, phosphates, and hexametaphosphates. The polyphosphonates specifically include, for example, the sodium and potassium salts of ethylene diphosphonic acid, the sodium and potassium salts of ethane 1-hydroxy-1,1-diphosphonic acid and the sodium and potassium salts of ethane-1,1,2-triphosphonic acid. Examples of these and other phosphorus builder compounds are disclosed in U.S. Patents 3,159,581; 3,213,030; 3,422,137; 3,400,176 and 3,400,148.

Water-soluble, non-phosphorus containing salts can also be selected for use herein as builders.

Specific examples of non-phosphorus, inorganic builders include water-soluble inorganic carbonate, bicarbonate and silicate salts. The alkali metal, e.g., sodium and potassium, carbonates, bicarbonates, and silicates are particularly useful herein.

Water-soluble, organic builders are also useful herein. For example, the alkali metal, ammonium and substituted ammonium polyacetates, carboxylates, polycarboxylates and polyhydroxysulfonates are useful builders in the present compositions and processes. Specific examples of the polyacetate and polycarboxylate salts include sodium, potassium, lithium, ammonium and substituted ammonium salts of ethylenediaminetetraacetic acid, nitrilotriacetic acid, oxydisuccinic acid, mellitic acid, benzene polycarboxylic acids, and citric acid.

Highly preferred non-phosphorus builders herein include sodium carbonate, sodium bicarbonate, sodium silicate, sodium citrate, sodium oxydisuccinate, sodium mellitate, sodium nitrilotriacetate, and sodium ethylenediaminetetraacetate, and mixtures thereof.

Additional preferred builders include the water-soluble salts, especially the sodium and potassium salts, of carboxymethyloxymalonate, carboxymethyloxysuccinate, cis-cyclohexanhexacarboxylate, cis-cyclopentanetetracarboxylate and phloroglucinol trisulfonate.

Another type of builder material useful in the present compositions and processes comprises a water-soluble electrolyte material which is capable of forming a water-insoluble reaction product with water hardness cations in combination with a crystallization "seed" which is capable of providing growth sites for said reaction product. "Seeded builder" compositions employing calcium carbonate as seed material are described in British Patent Specification 1,424,406.

More particularly, the seeded builders useful herein comprise a crystallization seed having a maximum particle dimension of less than 20 microns, preferably a particle diameter of from about 0.01 micron to about 1 micron, in combination with a material capable of forming a water-insoluble reaction product with free metal ions.

Many of the foregoing builder materials, e.g., the water-soluble carbonate salts, precipitate water hardness cations, thereby performing a builder function. Unfortunately, many of the precipitating builders used in detergent compositions do not reduce the free metal ion content of laundry baths quickly, and only complete with the organic detergent and the soil for the free metal ions. The result is that while some of the free metal ions are removed from the solution, some ions do react with the organic detergent and the soil, thereby decreasing the deterative action. The use of the crystallization seed quickens the rate of precipitation of the metal hardness ions, and softens the water before detergency performance can be adversely affected.

By using an electrolyte whose anion is capable of forming a water-insoluble product with water hardness cations in combination with a crystallization seed, the free metal ion concentration (hardness) of an aqueous laundering liquor can be reduced to less than 0.5 grains per gallon within about 120 seconds. In fact, the preferred seeded builders can reduce the free metal hardness to less than 0.1 grains/gallon with about 30 seconds.

Preferred seeded builders consist of: a water-soluble electrolyte which provides an anion capable of forming a reaction product having a solubility in water of less than about 1.4×10^{-2} wt.% (at 25°C) with divalent and polyvalent metal ions such as calcium, magnesium and iron; and a crystallization seed (0.001—20 micron diameter) which comprises a material which will not completely dissolve in water within 120 seconds at 25°C.

Specific examples of materials capable of forming the water-insoluble reaction product include the water-soluble carbonates, bicarbonates, sesquicarbonates, silicates, aluminates and oxalates. The alkali metal, especially sodium, salts of the foregoing materials are preferred for convenience and economy.

The crystallization seed employed in such seeded builders is preferably selected from the group consisting of calcium carbonate; calcium and magnesium oxalates; barium sulfate; calcium, magnesium and aluminum silicates; calcium and magnesium oxides; calcium and magnesium salts of fatty acids having 12 to 22 carbon atoms; calcium and magnesium hydroxides; calcium fluoride; and barium carbonate. Specific examples of such seeded builder mixtures comprise: 3:1 wt. mixtures of sodium carbonate and calcium carbonate having a 5 micron particle diameter; 2.7:1 wt. mixtures of sodium sesquicarbonate and calcium carbonate having a particle diameter of 0.5 microns; 20:1 wt. mixtures of sodium sesquicarbonate and calcium hydroxide having a particle diameter of 0.01 micron; and a 3:3:1 wt. mixture of sodium carbonate, sodium aluminate and calcium oxide having a particle diameter of 5 microns.

Non-builder electrolytes, e.g., sodium chloride, sodium bromide, potassium chloride, sodium sulfate and sodium nitrate, are useful herein at concentrations up to 65% by weight, and are especially useful for preparing high-electrolyte crutcher mixes in the manner described hereinafter.

The detergent compositions of this invention can contain all manner of other optional materials commonly employed in such compositions. For most purposes, such optional ingredients can comprise up to about 15% by weight of the total mix. The actual amount used will, of course, depend on the amount of any specific ingredient desired in the final composition.

Non-limiting examples of other optional ingredients which can be used in the detergent compositions herein include thickeners and soil suspending agents such as a carboxymethylcellulose. Various perfumes, optical bleaches, fillers, anti-caking agents and fabric softeners can be present to provide the usual benefits occasioned by the use of such materials in detergent compositions.

Perborate bleaches commonly employed in European detergent compositions can also be present as a component of the present detergent compositions, and are simply added thereto as dry admixtures.

Enzymes, especially the thermally stable proteolytic and lipolytic enzymes used in laundry detergents, can be admixed to the compositions in standard fashion.

As can be seen from the foregoing, the compositions herein can contain all manner of additive materials commonly recognized as being useful in laundry detergent compositions.

Processing

The detergent compositions herein can be prepared by simply admixing the methyl cellulose ether material to the remaining portions of the detergent compositions to provide the finished formulation. When the finished formulation is to contain substantial amounts of anionic surfactants, it is preferred that the cellulosic material be added thereto only in the presence of an electrolyte. Certain anionic surfactants can react with water-soluble cellulose derivatives to form a precipitate, and detergent compositions prepared from such mixtures can exhibit a decreased level of oily soil release benefits as compared with compositions prepared in optimal fashion. By preventing such interactions between the anionic surfactant and the cellulosic material, detergent compositions containing the methyl ether cellulose soil release agents can be provided which exhibit truly superior performance benefits.

Most commercial detergent compositions are prepared by a spray-drying process. In the preparation of spray-dried detergent granules, an aqueous mixture of the various components of the granules (the crutcher mix) is sprayed or otherwise introduced into what is essentially a drying tower. As the droplets of the crutcher mix proceed through the drying tower, the water is flashed off, and solid (semi-porous) detergent granules are secured. The advantages of spray-dried detergent granules over granules obtained by simple dry mixing of the individual ingredients is their homogeneity. That is to say, each granule contains the various ingredients in the same ratios and proportions introduced into the original crutcher mix. This provides obvious advantages over simple dry-mixed detergent formulations, inasmuch as dry mixing can result in non-homogeneity in the final detergent formulation such that the user is never certain of the composition of any given portion of such products.

Due to the foregoing considerations regarding the interaction of the cellulosic materials and anionic surfactants, the preparation of granular, anionic detergent compositions by a typical spray-drying process is preferably carried out in such fashion that the cellulosic material is added to the crutcher slurry containing both the anionic surfactant and the electrolyte.

It is most preferable herein to admix the cellulosic soil-release agent to the crutcher mix in a solid, particulate form. If it is desired to use a solution of the soil release agent, this can be done, but the solution will precipitate when it comes in contact with the electrolyte present in the crutcher mix; hence, there is little reason for pre-dissolving the cellulosic. In either case, the cellulosic is present as particles in the crutcher mix in combination with the electrolyte and anionic surfactant. Accordingly, it is intended that this pre-dissolution method, which results in the spontaneous re-formation of solid particles, be encompassed by the term "addition in solid form" as employed herein.

It is preferred that the electrolyte and soil release cellulosic materials herein be co-present in the detergent crutcher at a ratio of at least 1:1 by weight. However, inasmuch as the electrolyte materials are almost always present in large proportions, either as fillers or as detergency builders, whereas the soil release component is present in very minor proportions, this limitation is easily met.

Following the preparation of the aqueous crutcher mix in the foregoing manner, excess water is removed, conveniently, by heating at a temperature from 45°C to 100°C, to provide a substantially dry, homogeneous detergent composition. In a preferred mode, the slurry is dried by passage through a spray-drying tower at an air temperature from about 200°C to about 380°C, using conventional apparatus and techniques.

Spray-dried detergent compositions prepared in the foregoing manner contain the high DS methyl cellulose ether in an anionic surfactant-compatible form. Such compositions are added to an aqueous laundering liquor at a concentration of from 500 ppm to 10,000 ppm. Accordingly, the present invention encompasses a process for concurrently cleansing and providing a soil release finish to fabrics comprising contacting said fabrics with an aqueous solution containing from about 50 ppm to about 800 ppm of an anionic surfactant, from about 300 ppm to about 7000 ppm of an electrolyte and from about 5 ppm to about 200 ppm of a high DS methyl cellulose derivative of the type disclosed hereinabove for sufficient time (usually from 1 minute to 30 minutes) such that the cellulose material is affixed to the surface of the fabric.

Liquid detergent compositions comprising the high DS methyl cellulose soil release agent can be prepared by simply dissolving or suspending the cellulosic in a liquid carrier, preferably water or water-alcohol mixtures, and adding any suitable surfactant thereto. When anionic surfactants are employed in such compositions, it is preferred that an electrolyte, e.g., NaCl and KCl, be co-present therewith in the manner disclosed hereinabove for granular detergent composition.

The high DS methyl cellulose ethers employed in the instant detergent compositions are characterized by various parameters in the manner described immediately below. Specific examples of optimal high DS methyl cellulose soil release agents employed herein are set forth in Table 1 and 2, together with a tabulation of their effectiveness in releasing dirty motor oil (DMO) from polyester (P) and polyester/cotton (P/C) fabrics. The DMO data appearing in Table 1 are typical of the performance of the soil release cellulose herein in the granular detergent composition of Example I. The DMO release results appearing in Table

2 are typical of the results obtained using the cellulose ethers herein in the liquid detergent composition of Example II.

The DS (methyl) of the various cellulosic soil release agents employed herein can be determined in the manner set forth in "Methods in Carbohydrate Chemistry", III, Cellulose, R. L. Whistler, Ed., Academic Press, New York, 1963, Section 49, by I. Croon, at p. 277, *et seq.*

The gel point, or "closed point", of the high DS methyl cellulose ether soil release agents employed herein is determined in the following manner. A 2% wt. aqueous solution of the cellulose ether being tested is used to determine the gel point. Ten cc. of the 2% solution are placed in a test tube and a thermometer is inserted into the solution. The test tube containing the solution and thermometer is immersed in a beaker of water on a hot plate. The water is heated at a rate of approximately 1°C/minute. During this heating, the solution of cellulose ether is stirred with the thermometer. The temperature is raised, slowly, until the solution just becomes cloudy (the cellulose ethers exhibit a negative temperature coefficient of solubility). The temperature at which the solution clouds is the gel point of the cellulose ether being tested.

The viscosity of the high DS methyl cellulose ethers is determined on the basis of a 2% wt. aqueous solution in the manner disclosed in ASTM Standard D—2363 for the determination of the apparent viscosity of hydroxypropyl methyl cellulose. More specifically, a 2% water solution of the high DS methyl cellulose ether is determined in an Ubbelohde tube viscometer. The 2% solution is based on a dry mass of the product, i.e., the corrected mass for moisture found in the sample.

An accurately weighed sample of the cellulose ether (corrected for moisture content) is placed in an 8 oz. wide-mouth bottle. 98.0 Grams of hot water (85°C—90°C) are added to the 8 oz. bottle containing the 2 gram sample of cellulose ether. The mixture is agitated with a mechanical stirrer for 10 minutes, then placed in an ice bath (0°C—5°C) until the dissolution is complete. The stirrer assembly is equipped with a one hole stopper or bottle cap so that no water vapor is lost during this agitation time. The solution is deaerated, e.g., by centrifuging. When the solution is complete as evidenced by the absence of partially swollen or undispersed particles of cellulose ether, the viscosity is determined in a methyl cellulose viscometer at $20 \pm 0.1^\circ\text{C}$, in standard fashion.

The DP_w of the high DS methyl cellulose ethers can be experimentally determined in the following manner. As noted hereinabove, the DP_w of the cellulose is related to their viscosity. For determining DP_w , it is simplest to measure the viscosity of the cellulosic derivatives in cadoxen, which is a standard solvent for both substituted and unsubstituted cellulose. In general terms, the efflux time of a solution of a cellulosic derivative in 1:1 cadoxen water is measured in a Cannon-Ubbelohde dilution viscometer. The solution is diluted with additional solvent and the efflux time is again measured. The dilution step is repeated twice more, and the efflux times are again measured. The efflux time of the solvent is also determined in the same viscometer. From these data, the relative efflux time (or relative viscosity), the specific viscosity, and then the reduced viscosity are calculated. The reduced viscosity is plotted on linear graph paper vs. concentration of cellulose derivative in g/dl. A line is drawn through the points and extrapolated to zero concentration. The zero concentration intercept is defined as the intrinsic viscosity. The weight-average degree of polymerization, DP_w , can then be calculated by the Henley relationship as reported by Brown in the review article cited hereinabove.

More specifically, a clean Cannon-Ubbelohde dilution viscometer is placed in a 25°C bath and about 10 ml. of a 1:1 cadoxen-water mixture are added to the dilution bulb. The temperature is allowed to equilibrate. A nitrogen pressure cylinder is attached to the dilution bulb of the viscometer by flexible tubing. When the solution fills the bulb that allows suspended-level operation, the opening to this bulb is closed. The solution then enters the capillary and upper bulb. The nitrogen is disconnected when the fluid level passes the upper mark. The bulb is allowed to drain without timing to thoroughly coat all surfaces. The bulb is refilled following the same procedure until successive draining times agree within about 0.15 seconds. The temperature is maintained at $25.0 \pm 0.1^\circ\text{C}$ throughout the procedure. The viscometer is then emptied, rinsed thoroughly and dried.

The sample of the cellulosic derivative to be tested is conditioned to near equilibrium moisture (6%—10%) and the moisture is determined in standard fashion. The sample is then weighed accurately on an analytical balance and the weighed sample is transferred to a 4 oz. bottle. The bottle is fitted with a "Teflon"

(a Trade Mark) covered magnetic stirring with a length approximately 1/16 in. shorter than the diameter of the bottle. The stirring bar is placed in the bottle and the bottle is placed in ice water bath sitting on a magnetic stirrer base. Water is added, a drop at a time, to the bottle containing the cellulose sample. Each drop is directed on to the sample and only enough water is added to wet the sample with no excess in the bottom of the bottle. The volume of water used is recorded. The magnetic stirrer is turned on and the bar is allowed to rotate slowly. The wetted sample is allowed to chill at least five minutes.

Approximately 5 ml. of cadoxen are added to the wet sample. The exact volume used is noted. The bottle is then stoppered and stirred until all gels and fiber bundles disappear. For most samples, this stirring time is about one hour. The system is maintained at ice bath temperature throughout.

When the solution appears completely clear, enough cadoxen to give a total of 25.00 ml. of cadoxen is added. The stirrer speed is increased to provide vigorous stirring without spattering. Enough water is then added to give a total of 25.00 ml. of water. The mixture is allowed to stir until complete mixing is obtained, and the bottle is then removed from the bath and allowed to warm to room temperature.

Ten ml. of the above solution is transferred to the viscometer through the dilution bulb opening. The foregoing directions given for measuring the efflux time of a 1:1 cadoxen-water mixture are used to measure the efflux time of the solution. The bulb is always filled at least once before timing. The relative efflux time must be 1.8 or below. In order to achieve this, it is necessary to adjust the sample weight of cellulose employed. For example, for cellulosic compounds having DP_w of 300—600, the sample weight employed should be about 0.125 g/50 ml.; for a DP_w of 600—1000, ca. 0.10 g. of sample/50 ml. solvent is employed; for a DP_w of 1000—1500, ca. 0.05 g. of sample/50 ml. solvent is employed.

Either 3.0 or 5.0 ml. of the 1:1 cadoxen-water are then added to the opening of the dilution bulb. Nitrogen is bubbled through the solution for about a minute. The efflux time measurement is repeated. The addition of the diluent is repeated twice more, as above, and the efflux times are again measured.

Based on the data developed from the foregoing experimental procedure, the DP_w of the cellulose derivative is determined using the following relationships, wherein η is viscosity.

$$\eta_{rel} = \frac{t_{\text{solution}}}{t_{\text{solvent}}}$$

$$\eta_{sp} = \eta_{rel}^{-1}$$

$$\eta_{red} = \frac{\eta_{sp}}{\text{conc. in g/dl}}$$

The η_{red} is plotted vs. concentration of the cellulosic in g/dl on linear graph paper. A line is drawn through the points and extrapolated to zero concentration. The zero intercept (η) is used to calculated DP_w , as follows.

$$DP_w = \text{Antilog} \left(\frac{\log \left(\frac{(\eta)}{0.0184} \right)}{0.76} \right)$$

The following examples illustrate the detergent compositions of the present invention, but are not intended to be limiting thereof. As will be seen from the examples, the detergent compositions herein comprise from 5% to 99% by weight of a water-soluble organic surfactant of the type disclosed hereinabove containing at least 0.05%, preferably from 0.05% to 10%, more preferably from 0.25% to 1.5%, by weight of methyl cellulose ether. For purposes of economy, the compositions normally will contain from 10% to 35% by weight of the organic surfactant, but higher concentrations can be used, according to the desires of the formulator.

The methyl cellulose ethers employed in such detergent compositions preferably have a DS methyl in the range from 2.2 to 2.7, more preferably from 2.3 to 2.6. The gel point of the preferred methyl cellulose ethers is preferably less than 50°C, and most preferably lies within the range from 25°C to 48°C.

The viscosity of the methyl cellulose ethers usually lies within a range from 20

cps to 70,000 cps. For use in liquid detergent compositions having good flow properties, methyl cellulose ethers are selected having a viscosity from 20 cps to 250 cps (as a 2% wt. aqueous solution at $20 \pm 0.1^\circ\text{C}$).

The preferred cellulose ethers employed in the detergent compositions have a DP_w less than 1000, more preferably in the range from about 100 to about 1000.

Granular detergent compositions herein generally comprise from 10% to 35% by weight of a water-soluble anionic surfactant, from 10% to 80% by weight of an electrolyte builder, and at least 0.5% by weight of a methyl cellulose ether having a DS methyl of from 2.1 to 2.8. Most preferably, the methyl cellulose ethers employed in such compositions have a gel point below about 50°C . It is to be recognized that such granular detergent compositions can contain, in addition to the anionic surfactant, various nonionic surfactants such as the ethoxylated alcohols to provide additional oily soil release benefits and suds control properties. Such surfactant mixtures are well known in the art.

The liquid detergent compositions herein generally comprise from 5% to 50% by weight of a water-soluble surfactant, or mixtures of surfactants. Highly preferred liquid detergent compositions employ mixtures of anionic surfactants and nonionic surfactants such as the ethoxylated alcohols noted hereinabove. The liquid detergent compositions herein also contain from 0% to 10% by weight of electrolyte salts. These electrolyte salts are most often used when the liquid detergent compositions contain significant amounts (i.e., above 1%) of anionic surfactants in combination with nonionic surfactants such as the ethoxylated alcohols. The presence of the electrolyte salts prevents gelation of the surfactant mixtures on dilution with water. Moreover, the presence of the electrolyte salts prevents undesired interactions between the anionic surfactants and methyl cellulose ethers in the manner disclosed hereinabove. Liquid detergent compositions optimally contain at least 0.05% by weight of the methyl cellulose ethers having a DS methyl from about 2.1 to about 2.8. Fluidity of the liquid detergent compositions is provided by means of a liquid carrier, which comprises the balance of the composition. Liquid carriers useful herein include water and/or one or more C_1 — C_4 alcohols. Mixtures such as 10:1 (wt.) water:ethanol; 9:1 (wt.) water:isopropanol; and 20:1 (wt.) water:methanol can be employed as the carrier liquid.

As in the case of the granular detergent compositions herein, the liquid detergents preferably contain from 0.25% to 1.5% by weight of a methyl cellulose ether having a DS methyl of from about 2.3 to about 2.6. Most preferably, the methyl cellulose ether has a gel point below 50°C . To provide fluidity, the methyl cellulose ethers employed in the preferred liquid detergent compositions exhibit a viscosity in the range from 20 cps to 250 cps.

Highly preferred liquid detergent compositions herein comprise mixtures of a deterative nonionic surfactant, especially the ethoxylated primary and secondary alcohols having a hydrophilic/lipophilic balance (HLB) in the range of from 7 to 15, in combination with an alkanolamine-neutralized alkyl benzene sulfonate. Such mixtures of nonionic ethoxylated alcohols and alkanolamino-neutralized alkyl benzene sulfonates are known in the art.

More specifically, liquid detergent compositions comprising C_9 — C_{18} primary and secondary alcohols ethoxylated with from about 6 to about 12 moles of ethylene oxide, said ethoxylated alcohols having an HLB in the recited range, have been found to be especially useful in combination with alkanolamine-neutralized alkyl benzene sulfonates and free alkanolamines to prepare liquid detergent compositions containing the methyl cellulose soil release agents of the present invention. The alkanolamine-neutralized alkyl benzene sulfonates employed in such compositions include such materials as the mono-, and di- and tri-ethanolamine-neutralized alkyl benzene sulfonates wherein the alkyl group contains from about 9 to about 14 carbon atoms. The "free" alkanolamines, i.e., the alkanolamine present in the composition in excess of that needed to neutralize the alkyl benzene sulfonate, can be mono-, di- or tri-ethanolamine. Triethanolamine is preferred in such compositions, both as the counter ion for the alkyl benzene sulfonate and as the free alkanolamine in the liquid composition. It is to be understood that other water-soluble alkyl benzene sulfonates can be employed in the liquid compositions herein, e.g., the alkali metal alkyl benzene sulfonates, but the alkanolamine-neutralized alkyl benzene sulfonates, especially when employed in the presence of at least 1% by weight of the composition of free alkanolamine, provided superior performance benefits and are especially adapted for use in combination with the soil release ethers herein.

The liquid detergent compositions herein, especially those containing an ethoxylated alcohol nonionic surfactant, an alkanolamine-neutralized alkyl benzene sulfonate, and free alkanolamine, preferably contain 1% to 10% by weight of a water soluble electrolyte salt, especially potassium chloride, to prevent gelling of the product. Such compositions should also preferably contain at least 1% by weight of citrate anion which desirably prevents reddening of the product on contact with plastic bottles in the presence of atmospheric oxygen.

The dirty motor oil test (DMO) employed to test the soil release properties of the high DS methyl cellulose ethers clearly demonstrates the release benefits secured by treating a clean fabric with a detergent composition concurrently with said soil release ether. In general terms, the DMO test involves laundering fabric swatches in an aqueous bath using a detergent composition and the soil release ether being tested. The swatches are then rinsed thoroughly, and dried. The swatches are then stained with a measured amount of used automobile crankcase oil (DMO). The swatches are then re-laundered with the same detergent, but without the soil release ether. The DMO removal is determined gravi-metrically. Control tests can employ either detergent compositions without soil release agents, or detergent-plus-soil release agents. For convenience and to assure that particle size is not a factor in the test, the soil release ethers can be added to the aqueous laundry bath as aqueous solutions.

EXAMPLE I.

	<u>Ingredient</u>	<u>Weight %</u>	
	"Tergitol" 15—S—9*	12	
25	Sulfated tallow alcohol, sodium salt	2	25
	Linear alkyl benzene sulfonate, sodium salt (alkyl = C _{11.8} avg.)	2	
30	"Tergitol" 15—S—3*	8	30
	Sodium carbonate	30	
	Calcium carbonate (microfine seeds)	9	
	Sodium sulfosuccinate	2	
35	Sodium toluene sulfonate	2	35
	Soluble silicates (2.0 ratio)	10	
	Kaolinite clay (microfine)	5	
	Sodium sulfate	7.7	
	Powdered amorphous silica	5	
40	Optical brightener, perfume, coloring agent, water and minors	Balance	40

*Commercial nonionic surfactants comprising a mixture of C₁₀—C₁₅ secondary alcohols ethoxylated with an average of 9 and 3 moles of ethylene oxide, respectively.

45 The word "Tergitol" is a Trade Mark. 45

The detergent composition of Example I is prepared by admixing the nonionic surfactant together with the kaolinite clay and heating to a temperature of *ca.*

150°F. The hot nonionic/clay mixture is then admixed with the remaining ingredients (exclusive of the silica) in an aqueous crutcher and spray-dried in the manner set forth in British Patent Application 44606/74 (Specification Serial No. 1,460,646) and also in West German Offenlegungsschrift 2,448,502. The silica is then dusted on the spray-dried granules as a free-flow agent.

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0.84 Gram of the detergent composition of Example I is added to 0.7 liters of water in a Tergotometer, together with 0.0084 gram of the high DS methyl cellulose ether corresponding to cellulose ether 4 appearing in Table 1. The laundry bath is used to launder fabrics in the manner set forth hereinabove for the DMO test. Typical results from the test are shown in Table 1. As can be seen from the table, the detergent composition of Example I together with the high DS methyl soil release ether 4 provides excellent DMO release from polyester fabrics and is substantially better than the control cellulosic in the release of DMO from polyester-cotton blend fabrics.

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The test procedure employing the detergent composition of Example I is repeated using cellulose ethers B, C, D, E, F, G and H appearing in Table 1, respectively. As seen from the data in Table 1, the soil release ethers herein provide truly superior DMO release from both pure polyester and blended fabrics.

TABLE 1

Cellulose Ether	DS (Methyl)	DP _w	Viscosity (cp)	Gel Pt. (°C)	% DMO Release	
					P/C	P
A	2.31	418	4,515	40	39	82
B	2.29	419	1,185	39	37	80
C	2.22	1,113	1,399	48	31	79
D	2.14	386	94	38	27	76
E	2.28	1,005	26,000	39	29	78
F	2.40	813	27,000	39	30	78
G	2.62	517	5,619	37	32	81
H	2.45	167	93	30	31	80
Control	1.99	1,760	1,260	51	27	37

In the "% DMO Release" column "P/C" denotes polyester-cotton blend and "P" polyester fabrics.

EXAMPLE II.

	Ingredient	Weight %	
	Neodol 45—7*	33	
5	Alkyl benzene sulfonate (acid form)	16.5	5
	Triethanolamine	11.0	
	Potassium chloride	2.5	
	Citric acid	0.25	
	Ethyl alcohol	5.0	
10	Water and minors	Balance	10

*Commercial nonionic surfactant comprising a mixture of primarily C_{14} — C_{15} alcohols ethoxylated with an average of about 7 moles of ethylene oxide per mole of total alcohol.

15	The detergent composition of Example II is prepared by simply admixing the components in the proportions indicated. 0.84 Gram of this detergent composition is added to 0.7 liters of water in a Tergotometer, together with 0.0084 gram of soil release ether <i>A</i> appearing in Table 2. The laundering liquor is used to assess the DMO release properties of the cellulose ether in the DMO test disclosed above.	15
20	The results from the test, which show the superior performance properties of soil release ether <i>A</i> in a liquid detergent composition as compared with a low DS cellulosic, are set forth in Table 2.	20
25	The test procedure employing the detergent composition of Example II is repeated using cellulose ethers <i>B</i> , <i>C</i> , <i>D</i> , <i>E</i> , <i>F</i> , <i>G</i> , and <i>H</i> , appearing in Table 2, respectively. As seen from the data in Table 2, the soil release ethers herein provide truly superior DMO release from both pure polyester and blended fabrics.	25

TABLE 2

Cellulose Ether	DS (Methyl)	DP _w	Viscosity (cp)	Gel. Pt. (°C)	% DMO Release	
					P/C	P
A	2.31	418	4,515	40	34	87
B	2.29	419	1,185	39	29	86
C	2.22	1,113	1,399	48	30	84
D	2.14	386	94	38	27	84
E	2.28	1,005	26,000	39	23	85
F	2.40	813	27,000	39	25	86
G	2.62	517	5,619	37	25	85
H	2.45	167	93	30	29	85
Control	1.99	1,760	1,260	51	26	70

In the "% DMO Release" column "P/C" denotes polyester-cotton blend and "P" polyester fabrics.

EXAMPLE III.

A spray-dried detergent composition containing a high DS methyl cellulose ether is as follows.

	5	Ingredient	Weight %	
			5	10
5		Linear alkyl benzene sulfonate, sodium salt (alkyl = C _{11.8} avg.)	10	
		Sodium tripolyphosphate	50	
		Sodium sulfate	20	
		Sodium sulfosuccinate	5	
10		Soil release ether*	1.5	
		Water and minors	Balance	

*High DS methyl cellulose ether corresponding to ether A from Table I.

The composition of Example III is prepared by admixing all ingredients exclusive of the soil release ether in an aqueous crutcher mix at a ratio of ingredients:water in the mix of 1:1, by weight. After all ingredients have been homogeneously distributed throughout the crutcher mix by stirring, and the electrolytes have all dissolved, the soil release ether is added to the mix in the form of a solid which will pass through a 100 mesh sieve. The crutcher mix is stirred until the particles of soil release ether are uniformly distributed throughout, and is then spray-dried at an average air temperature of *ca.* 280°C. The resulting product is in the form of substantially dry, solid, non-caking, homogeneous detergent granules.

An aqueous laundering bath comprising 0.35% by weight of the detergent granules of Example III is prepared. Eight gallons of the bath are employed to launder a 5 lb. load of cotton and polyester fabrics (10 minute laundry time). The laundry bath temperature is maintained around 55°C and the pH is *cs.* 10.0. The fabrics are then rinsed thoroughly and dried. The fabrics are provided with a soil release finish which facilitates removal of oily hydrocarbon soils in subsequent launderings.

The procedure of Example III is followed with polymers *B, C, D, E, F, G,* and *H* of Table 1, respectively, being substituted in an equivalent amount for soil release ether *A*. Equivalent oily soil release properties of the laundered fabrics are secured.

In the composition of Example III the linear alkyl benzene sulfonate surfactant is replaced by an equivalent amount of tallowalkyl sulfate, sodium salt; coconutalkyl glycerol sulfonate, sodium salt; mixed alkyl ether (ethoxylated) sulfate (sodium salt) wherein the alkyl moiety is mixed C₁₄—C₁₈ and wherein the average degree of ethoxylation is *ca.* 3; mixed C₁₄—C₁₆ olefin sulfonate, sodium salt form; and C₁₄—C₁₈ sodium soap, respectively, and equivalent soil release is secured with the high DS methyl ethers *A* to *H* set forth herein in Table 1.

In the composition of Example III the sodium tripolyphosphate builder is replaced by an equivalent amount of sodium carbonate, sodium bicarbonate, sodium silicate, sodium citrate, sodium oxydisuccinate, sodium mellitate, sodium nitrilotriacetate, and sodium ethylenediaminetetraacetate, respectively, and equivalent results are secured.

EXAMPLE IV.

A liquid detergent composition containing a high DS methyl cellulose ether is as follows.

Ingredient	Weight %
Coconut alcohol ethoxylate (9)	30
Linear alkyl benzene sulfonate, triethanolamine salt (alkyl = C _{11.8} avg.)	10
Potassium chloride	3
Triethanolamine	3
Triethanolammonium citrate	2
Ethyl alcohol	5
Soil release ether*	1.0
Water and Minors	Balance

*High DS methyl ether corresponding to ether *D* appearing in Table 2.

The composition of Example IV is prepared by admixing all ingredients, exclusive of soil release ether *D*, and agitating the mixture until all electrolytes are dissolved. Soil release ether *D* is then admixed with the solution in the form of a dry powder which passes through a 150 mesh standard sieve. The resulting

composition is in the liquid state and is easily pourable. The composition is found not to redden on contact with plastic bottles and does not gel when diluted with water.

The composition of Example IV is added to an aqueous laundering bath at a concentration of 0.20% (wt.), at a temperature of 55°C, water hardness 7 grains/gallon, and a pH of 10.0. Polyester and mixed polyester/cotton fabrics are laundered in the bath for a period of 10 minutes, after which the fabrics are thoroughly rinsed with fresh water and dried at ambient temperatures. The fabrics are provided with a soil release finish.

In the composition of Example IV, soil release ether *D* is replaced by an equivalent amount of soil release ethers *A*, *B*, *C*, *E*, *F*, *G*, and *H*, from Table 2, respectively, and equivalent soil release performance is secured.

In the composition of Example IV, the coconut ethoxylate is replaced by an equivalent amount of the following ethoxylated nonionic surfactants having an HLB in the range of from 7 to 15, respectively, and equivalent detergency performance is secured. In the listed nonionic surfactants, the integer in parentheses represents the average number of moles of ethylene oxide condensed per mole of alcohol or alkyl phenol. The nonionic surfactants are as follows: *p*-nonylphenol EO(6); 1-decanol EO(6); 1-tetradecanol EO(7); 1-octadecanol EO(8); 2-tetradecanol EO(6); and 2-octadecanol EO(6).

In the composition of Example IV the free triethanolamine is replaced by an equivalent amount of free monoethanolamine and free diethanolamine, respectively, and equivalent results are secured.

In the composition of Example IV the triethanolamine-neutralized alkyl benzene sulfonate surfactant is replaced by an equivalent amount of monoethanolamine-neutralized alkyl benzene sulfonate and diethanolamine-neutralized alkyl benzene sulfonate, respectively, and equivalent results are secured.

The composition of Example IV is reformulated to contain a total of 50% by weight of the combination of nonionic ethoxylated surfactant and triethanolamine-neutralized alkyl benzene sulfonate. While the total amount of mixed surfactant is maintained constant, the product is reformulated at a weight ratio of nonionic:anionic surfactant of 5:1, 4:1, 3:1, 2:1, and 1:1, respectively. Excellent oily soil removal and release is secured with compositions formulated at these surfactant ratios and employing the high DS methyl celluloses set forth in Table 2.

WHAT WE CLAIM IS:—

1. A detergent composition, having soil release properties, comprising:

(a) from 5% to 99% by weight of a water soluble organic detergent selected from anionic, nonionic, zwitterionic and ampholytic detergents and mixtures thereof; and

(b) at least 0.05% by weight of a methyl cellulose ether having a D.S. methyl of at least 2.1, provided that when the composition is in liquid form, the methyl cellulose must have a viscosity of from 20 to 250 centipoises (as a 2% wt. aqueous solution at $20 \pm 0.1^\circ\text{C}$.)

2. A composition according to claim 1, in which the methyl cellulose ether has a D.S. methyl of 2.1 to 2.8.

3. A composition according to claim 2, in which the methyl cellulose ether has a D.S. methyl of 2.2 to 2.8.

4. A composition according to claim 3, in which the methyl cellulose ether has a D.S. methyl of 2.3 to 2.6.

5. A composition according to any of claims 2 to 4 in which the methyl cellulose ether has a gel point less than 50°C.

6. A granular composition according to claim 5 in which the methyl cellulose ether has a viscosity of from 20 cps to 70,000 cps (as a 2% wt. aqueous solution at $20 \pm 0.1^\circ\text{C}$) and a DP_w of less than 1,000.

7. A composition according to claim 6 in which the methyl cellulose ether has a D.S. methyl of from 2.3 to 2.6, a gel point from 25°C to 48°C and a DP_w of from 400 to 800.

8. A granular detergent composition according to any of claims 2 to 7 comprising:

(a) from 10% to 35% by weight of water soluble anionic surfactant;

(b) at least 0.5% by weight of methyl cellulose ether having a D.S. methyl of from 2.1 to 2.8; and

(c) from 10% to 80% by weight of an electrolyte builder.

9. A liquid detergent composition according to any of claims 2 to 7 comprising:

from 5% to 50% by weight of a surfactant or mixture of surfactants;
up to 10% by weight of electrolyte builder; and a liquid carrier.

10. A composition according to claim 9, in which the liquid carrier is water
and/or one or more C₁—C₄ alcohols.

5 11. A composition according to any of claims 9 or 10 in which the surfactant
comprises a mixture of an ethoxylated alcohol having HLB from 7 to 15 and an
alkanolamine-neutralised alkyl benzene sulphonate. 5

12. A composition according to claim 11, which comprises from 1% to 10% of
a water-soluble electrolyte salt.

10 13. A detergent composition according to claim 1, having soil release
properties, substantially as herein described in any one of the Examples. 10

14. A method for concurrently cleansing and imparting soil-release properties
to fabrics which comprises contacting said fabrics with an aqueous laundry
medium containing 500 ppm to 10,000 ppm of a composition according to any of
claims 1 to 13. 15

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